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SYNTHESIS OF CATENATED POLYNITROGEN COMPOUNDS

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[a]RAYTHEON ITSS CORPORATION

PROGRAM OVERVIEW

- SYNTHESIS OF NOVEL MONOPROPELLANTS CONSISTING OF HIGHLY ENDOTHERMIC POLYNITROGEN ALLOTROPES

- USE TECHNIQUES DEVELOPED IN SYNTHESIS OF OTHER ENERGETIC MATERIALS TO PURSUE CATENATED RATHER THAN POLYCYCLIC POLYNITROGEN COMPOUNDS

  RING CLOSURE REACTIONS FOR POLYCYCLIC COMPOUNDS ARE UNKNOWN AND DIFFICULT TO ENVISION

  IN CONTRAST, ONE CAN CONCEIVE OF REACTIONS THAT MIGHT LEAD TO CATENATED COMPOUNDS

- USE THEORY AND CALCULATIONS TO GUIDE SYNTHESIS EFFORTS
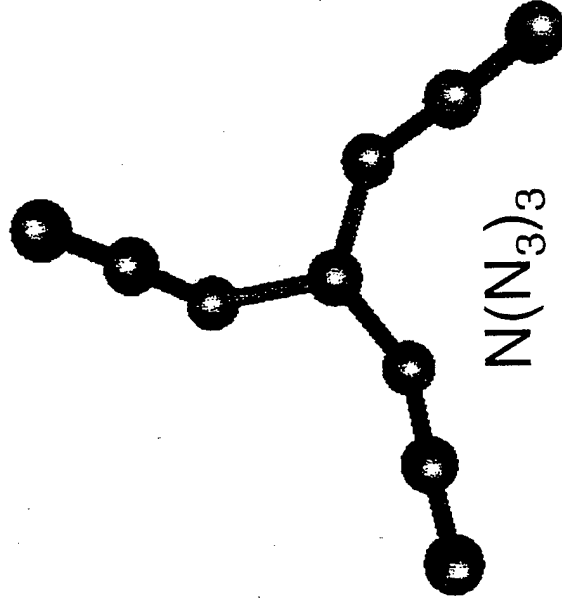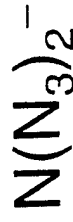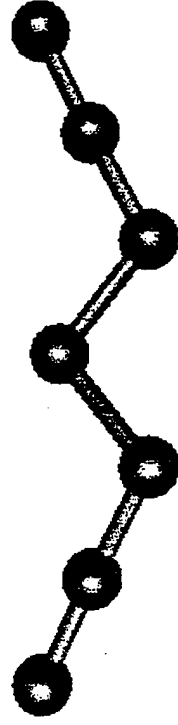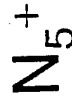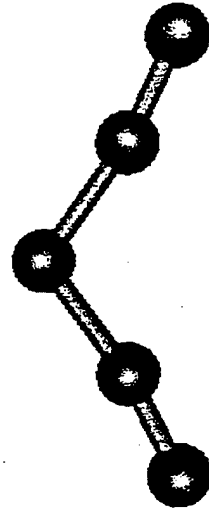
- HIGH-RISK, HIGH-PAYOFF PROGRAM

  PROPOSED COMPOUNDS ARE EXTREMELY ENERGETIC

  STABILITY OF ENERGETIC MATERIALS TYPICALLY DECREASES WITH INCREASING ENDOTHERMICITY

CALCULATIONS ON CATENATED POLYNITROGEN SPECIES

- HAVE DEMONSTRATED THE FEASIBILITY OF

N_5^+

$N(N_3)_3$

$N(N_3)_2^-$

$N(N_3)_4^+$
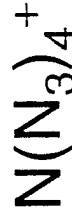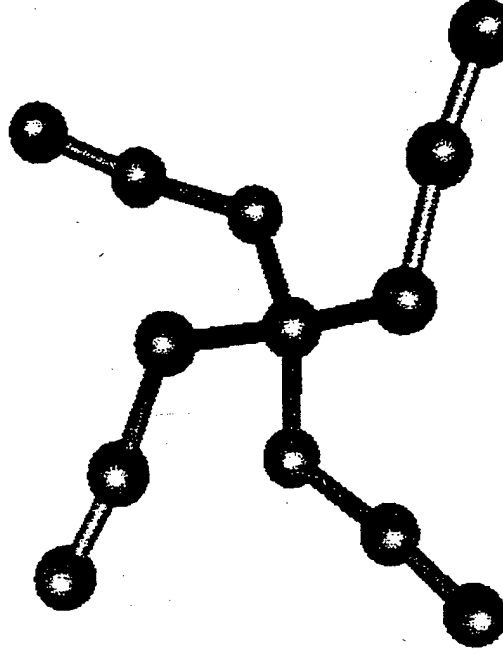
- AB INITIO CALCULATIONS SHOW THESE SPECIES TO BE VIBRATIONALLY STABLE

STATE OF THE ART IN HOMOLEPTIC CATENATED POLYNITROGEN COMPOUNDS

- ONLY TWO COMPOUNDS KNOWN WHICH CAN BE PREPARED "IN BULK"

  N_2 LONG KNOWN, BUT FIRST ISOLATED IN PURE FORM ONLY IN

  1772 INDEPENDENTLY BY

  RUTHERFORD

  SCHEELE

  CAVENDISH

  AZIDE, N_3^-, DISCOVERED IN 1890 BY

  CURTIUS

- THE ABSENCE OF ANY OTHER SUCH COMPOUND IS A TESTIMONY TO THE

  PROBLEMS THAT CAN BE EXPECTED FOR THE SYNTHESIS OF NEW

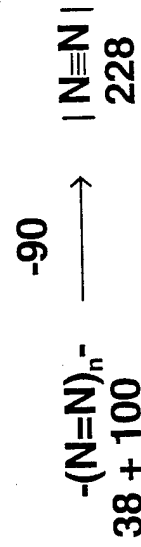 POLYNITROGEN COMPOUNDS

SYNERGISM OF THEORY AND SYNTHESIS

- AFRL HAS EXCELLENT CAPABILITIES IN BOTH THEORY AND SYNTHESIS

    THANKS TO AFOSR PROGRAM

- QUANTUM-CHEMICAL CALCULATIONS ARE USED TO IDENTIFY PROMISING

    CANDIDATES AND HELP CHARACTERIZE NEW COMPOUNDS

    INFRARED SPECTRA, RAMAN SPECTRA, AND NMR CHEMICAL SHIFTS

    DECOMPOSITION PATHWAYS AND ENERGY BARRIERS

    THERMODYNAMIC PROPERTIES

    PROPELLANT SPECIFIC IMPULSE

- GENERAL APPROACH TO SYNTHESIS OF PROMISING CANDIDATES

    SYNTHESIZE COMPOUNDS ON A VERY SMALL SCALE

    IDENTIFY AND CHARACTERIZE THE NEW COMPOUNDS

    GET SENSITIVITY DATA AND PHYSICAL PROPERTIES

    SCALE UP THE SYNTHESIS OF VIABLE NEW MATERIALS

PROBLEMS WITH SYNTHESIS OF POLYNITROGEN HEDM

- ALL THE ENERGY MUST COME FROM ENDOTHERMICITY WHICH MAKES

  POLYNITROGEN HEDM EXTREMELY DANGEROUS

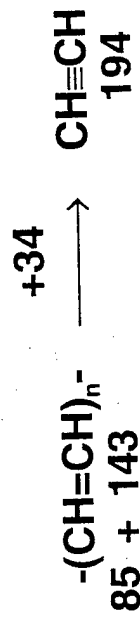- BASIS FOR HIGH ENERGY CONTENT ARE THE LARGE DIFFERENCES IN BOND

  ENERGIES FOR N-N BONDS

N-N	38 kcal/mol		C-C	85 kcal/mol
N=N	100 kcal/mol		C=C	143 kcal/mol
N≡N	228 kcal/mol		C≡C	194 kcal/mol

$$-(N=N)_n- \xrightarrow{-90} \; |N≡N| $$
$$38 + 100 \qquad\qquad 228$$

$$-(CH=CH)_n- \xrightarrow{+34} \; CH≡CH$$
$$85 + 143 \qquad\qquad 194$$

EXCEPTIONS: N_2, O_2 NORMAL CASE:

STABLE MONOMERS   STABLE POLYMERS
UNSTABLE POLYMERS   UNSTABLE MONOMERS

# GENERAL CONCEPT FOR POLYNITROGEN HEDM SYNTHESIS

- ALL POLYNITROGEN COMPOUNDS ARE UNSTABLE WITH RESPECT TO N_2

- ACTIVATION ENERGY BARRIER TOWARD N_2 ELIMINATION IS DETERMINED

  BY THE WEAKEST BOND IN POLYNITROGEN COMPOUND

- THE BARRIER AND METASTABILITY OF POLYNITROGEN COMPOUNDS MUST

  BE INCREASED BY SUITABLE RESONANCE STRUCTURES

  $$[\; |N{-}N{\equiv}N|\;]^- \longleftrightarrow [\; N{=}N{=}N \;]^- \longleftrightarrow [\; |N{\equiv}N{-}N|\;]^-$$

- DOUBLE BOND CHARACTER OF N-N BONDS IN AZIDE ION EXPLAINS ITS

  EXCEPTIONAL STABILITY

- HOW CAN THIS STABILIZATION EFFECT BE TAKEN ADVANTAGE OF?

EXPANSION OF THE AZIDE STRUCTURE

- ADDITION OF $[N_3]^+$ UNITS TO N_3^-

$$[N=N=N]^- + [N]^+ \longrightarrow N=N=N=N$$
$$N_4$$

$$N=N=N + [N]^+ \longrightarrow [N=N=N=N=N]^+$$
$$N_5^+$$
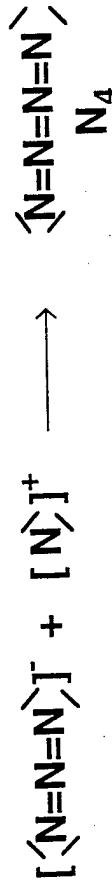
- HOWEVER, THEORETICAL CALCULATIONS SHOW THAT $D_{\infty h}$ N_4 IS NOT STABLE

NEIGHBORING CHARGES OF EQUAL SIGN MUST BE AVOIDED

$$N=N=N=N$$
$$(-)\,(+)\,(+)\,(-)$$

- NO PLAUSIBLE RESONANCE STRUCTURES CAN BE WRITTEN FOR N_4 WHICH RETAIN DOUBLE BOND CHARACTER WHILE AVOIDING NEIGHBORING CHARGES OF EQUAL SIGN
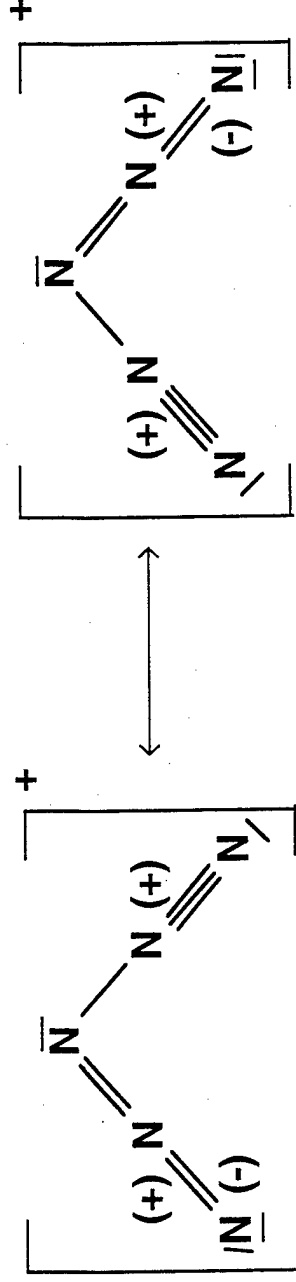
EXPANSION OF THE AZIDE STRUCTURE TO N_5^+

- **THE SAME PROBLEM EXISTS FOR N_5^+ WITH NEIGHBORING POSITIVE CHARGES**

$$\left[N{=}N{=}N{=}N{=}N \right]^+$$
$$(-)\ (+)\ (+)\ (+)\ (-)$$

- **RESONANCE STRUCTURES, HOWEVER, CAN BE WRITTEN WHICH AVOID THIS PROBLEM**

- **AB INITIO CALCULATIONS (CCSD(T) AND B3LYP) CONFIRM THE STABILITY OF THIS C_{2v} STRUCTURE**

SELECTION OF SUITABLE STARTING MATERIALS FOR N_5^+ SYNTHESIS
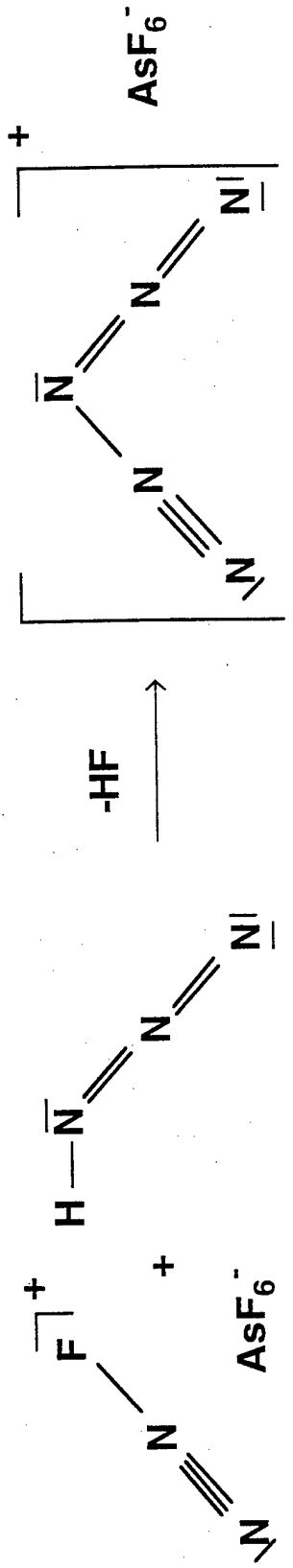
- REQUIREMENTS

  STARTING FRAGMENTS MUST HAVE ALREADY BUILT IN WEAKENED BONDS

  MUST HAVE A FORMAL POSITIVE CHARGE (IP OF N_2 = 359 kcal/mol)
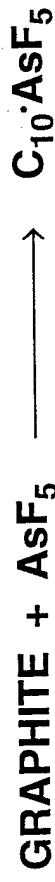
  COUPLING REACTION MUST BE EXOTHERMIC

  CHOICE OF SUITABLE SOLVENT (HEAT SINK, STABILIZATION, SAFETY)

- IDEAL CANDIDATE SYSTEM

SYNTHESIS OF $N_2F^+MF_6^-$ (M = As, Sb) STARTING MATERIAL

- **KNOWN SYNTHESIS**

  $$\text{GRAPHITE} + AsF_5 \longrightarrow C_{10}\cdot AsF_5$$

  $$2\,C_{10}\cdot AsF_5 + N_2F_4 \longrightarrow 2\,C_{10}^{+}AsF_6^- + trans\text{-}N_2F_2$$

  $$trans\text{-}N_2F_2 \longrightarrow cis\text{-}N_2F_2$$

  $$cis\text{-}N_2F_2 + MF_5 \longrightarrow N_2F^{+}MF_6^- \quad (M = As,\ Sb)$$

- **ATTEMPTS TO SIMPLIFY $N_2F^+MF_6^-$ SYNTHESIS WERE UNSUCCESSFUL**

  $$N_2 + F_2 + SbF_5 \longrightarrow N_2F^{+}SbF_6^-$$

  (VARYING TEMPERATURES AND PRESSURES)

  (METHOD COMPARABLE TO SUCCESSFUL SYNTHESIS OF $NF_4^{+}SbF_6^-$)

  $$NF_3 + F_2 + SbF_5 \longrightarrow NF_4^{+}SbF_6^-$$

  (250 °C AND 150 ATM PRESSURE)

ACTUAL SYNTHESIS OF $N_5^+ AsF_6^-$

- ## SYSTEM WORKED AS PLANNED

$$N_2F^+AsF_6^- + HN_3 \xrightarrow[-78^\circ C]{HF} N_5^+AsF_6^- + HF$$
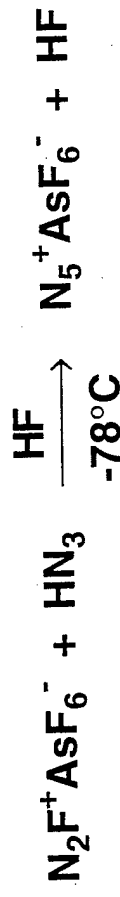
HIGH YIELD

ONLY OTHER BYPRODUCT 20-40% $H_2N_3^+AsF_6^-$

2 MMOL (0.5 G) SCALE

- ## PROPERTIES OF $N_5^+AsF_6^-$

WHITE SOLID WHICH IS SPARINGLY SOLUBLE IN HF

MARGINALLY STABLE AT 22°C

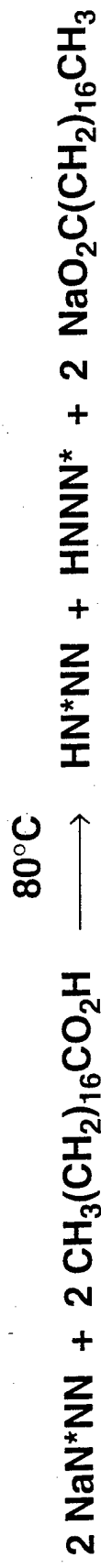HIGHLY ENERGETIC, REACTS VIOLENTLY WITH WATER AND ORGANICS

CALCULATED $\Delta H_f^\circ N_5^+{}_{(g)}$ = 353 kcal/mol
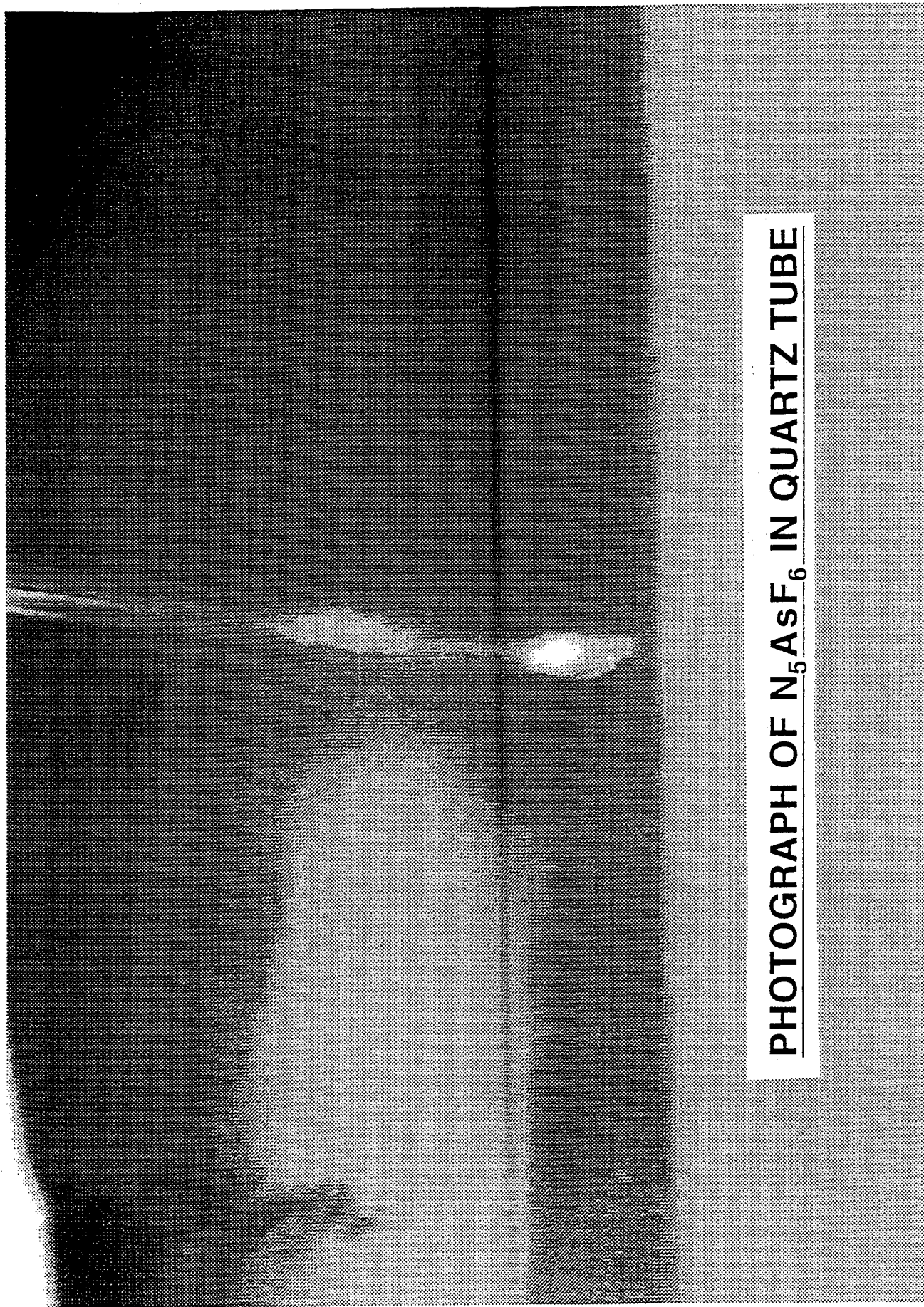
POWERFUL OXIDIZER

1st I.P. OF O_2 = 288 kcal/mol
1st I.P. OF N_2 = 359 kcal/mol

SYNTHESIS OF ^{15}N LABELED $N_5^+AsF_6^-$

$$2\ NaN^*NN + 2\ CH_3(CH_2)_{16}CO_2H \xrightarrow{80°C} HN^*NN + HNNN^* + 2\ NaO_2C(CH_2)_{16}CH_3$$

$$2\ N_2F^+AsF_6^- + HN^*NN + HNNN^* \longrightarrow [N^*NNNN]^+AsF_6^- + [NNN^*NN]^+AsF_6^- + 2\ HF$$

^{15}N LABELED N_5AsF_6 NEEDED FOR POSITIVE IDENTIFICATION OF N_5^+ BY SPECTROSCOPIC METHODS

PHOTOGRAPH OF N$_5$AsF$_6$ IN QUARTZ TUBE

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CHARACTERIZATION OF $N_5^+AsF_6^-$
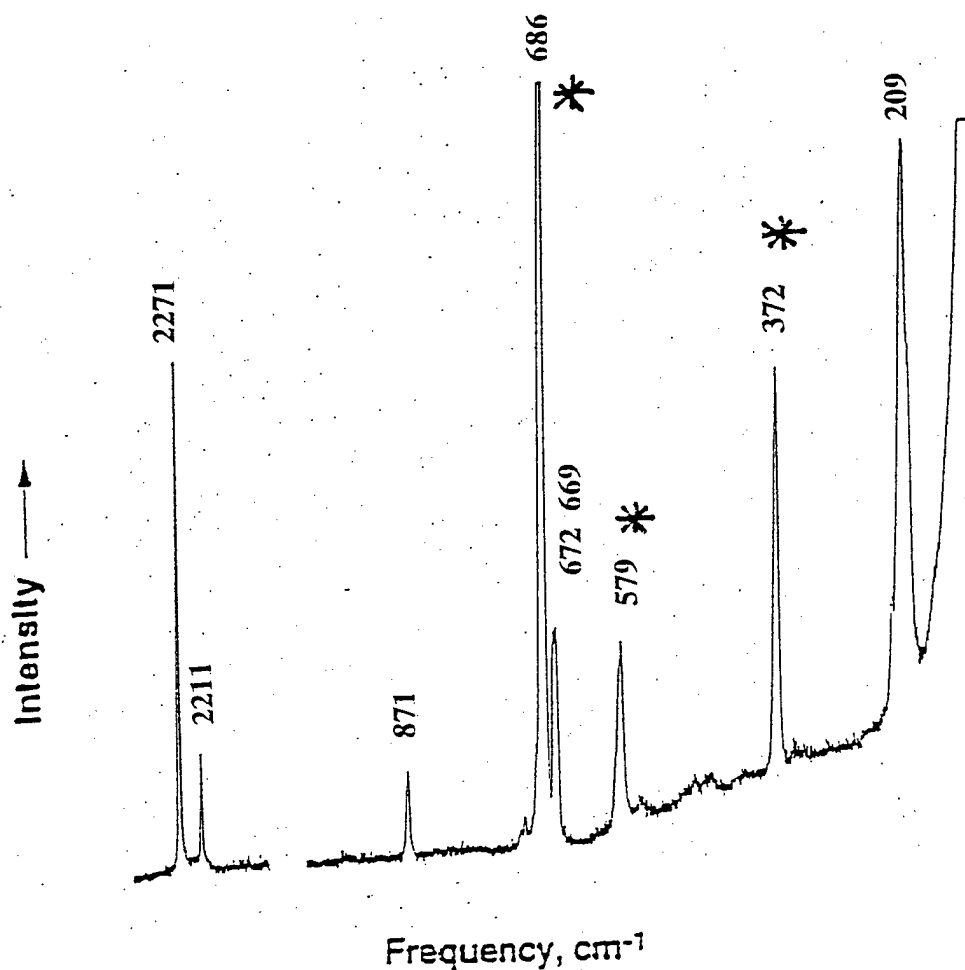
- ^{14}N AND ^{15}N NMR SPECTRA

- LOW-TEMPERATURE RAMAN AND INFRARED SPECTRA OF NORMAL AND ISOTOPICALLY LABELED N_5^+

- NORMAL COORDINATE ANALYSIS

- MASS SPECTROSCOPY

- THEORETICAL CALCULATIONS

  OPTIMIZED GEOMETRY
  VIBRATIONAL SPECTRA
  ISOTOPIC SHIFTS
  NMR SHIFTS
  HEAT OF FORMATION

OPTIMIZED GEOMETRIES FOR N_5^+ CCSD(T) (B3LYP) VALUES

$[^{14}N-^{14}N-^{14}N-^{14}N-^{14}N]^+ AsF_6^-$
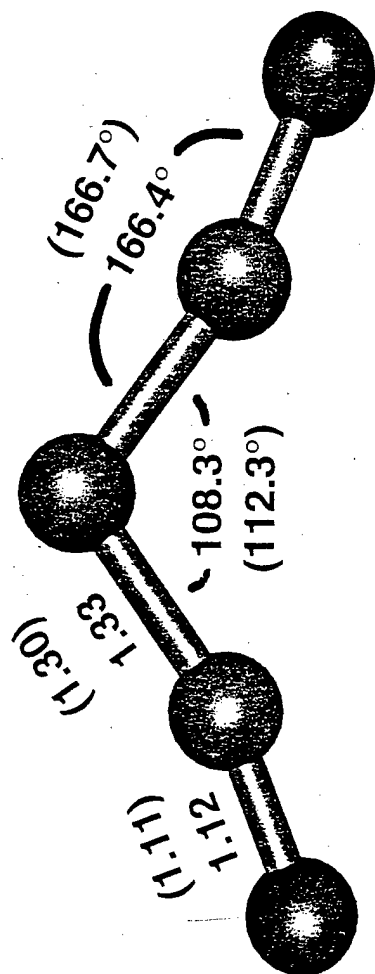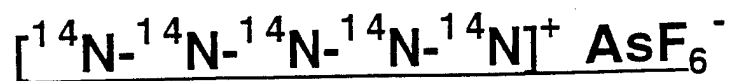
LOW-TEMPERATURE RAMAN SPECTRUM

* = AsF_6^-

Frequency, cm^{-1}

N_5^+	OBSD (cm^{-1})	CCSD(T) (cm^{-1})	B3LYP (cm^{-1})
ν_1 (A1)	2271	2229	2336
ν_7 (B2)	2211	2175	2282
ν_2 (A1)	871	818	850
ν_4 (A1)	209	181	193

$[^{15}N-^{14}N-^{14}N-^{14}N-^{14}N]^+ AsF_6^-$

$[^{14}N-^{14}N-^{15}N-^{14}N-^{14}N]^+ AsF_6^-$

LOW-TEMPERATURE
RAMAN SPECTRUM

14N-15N SHIFTS (cm^{-1})

	OBSD	CALCD
ν_1	12	11.8
ν_7	21	21.4
ν_2	14	14.1

Intensity →

Frequency, cm^{-1}

2271
2259
2211
2190
869
855

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NITROGEN NMR SPECTRA OF

$[^{15}N\text{-}^{14}N\text{-}^{14}N\text{-}^{14}N\text{-}^{14}N]^+$ AND $[^{14}N\text{-}^{14}N\text{-}^{15}N\text{-}^{14}N\text{-}^{14}N]^+$

$* = [H_2N\text{-}\underline{N}\text{-}N]^+$

N_3

N_2

N_1

^{15}N

^{14}N

^{15}N
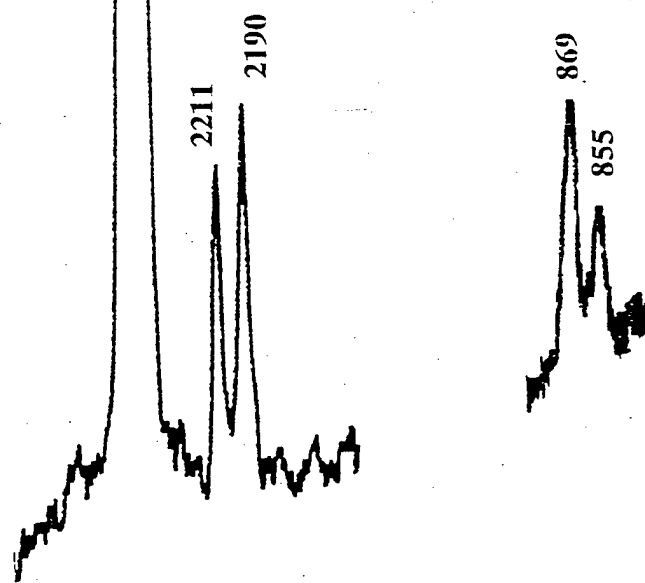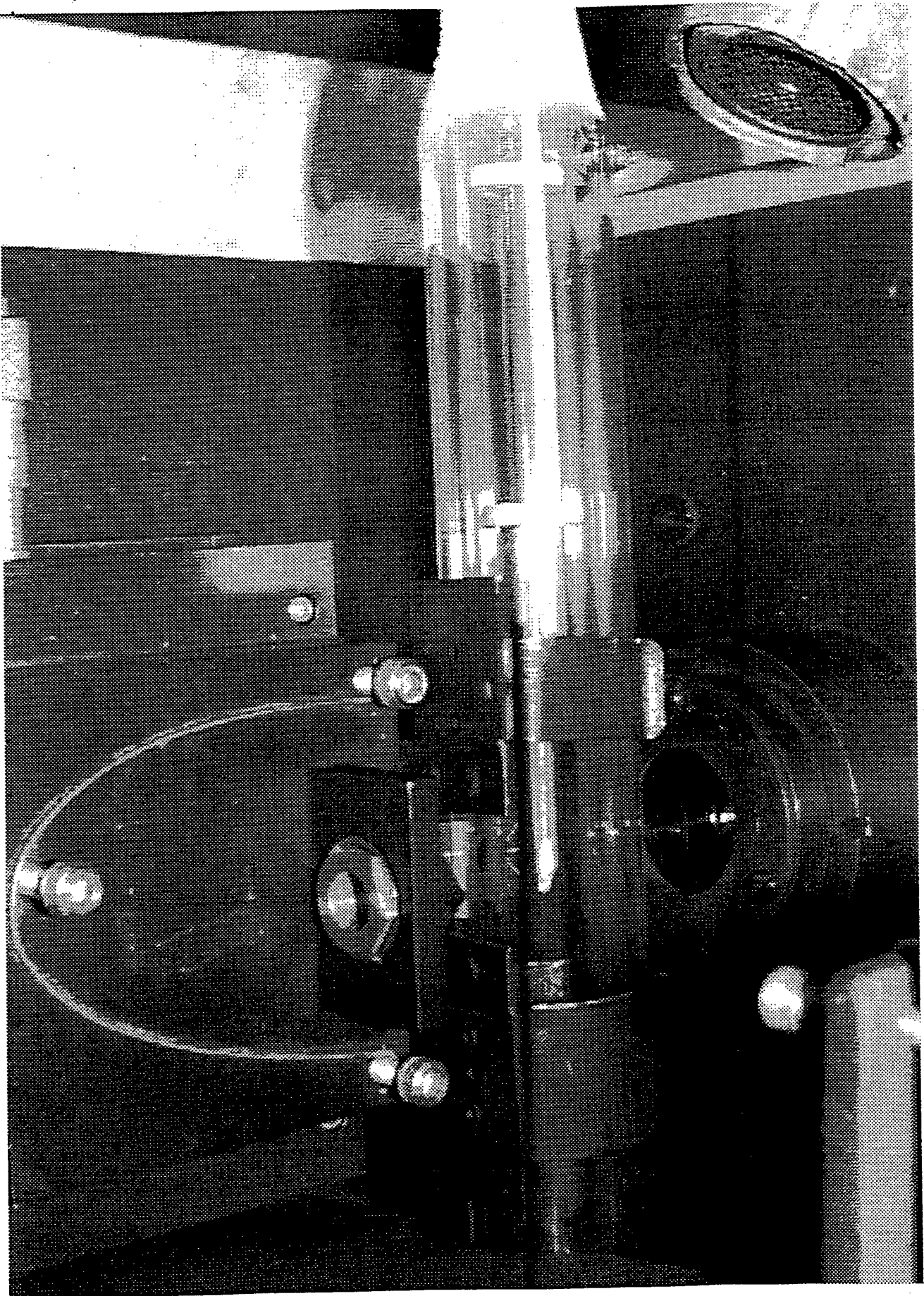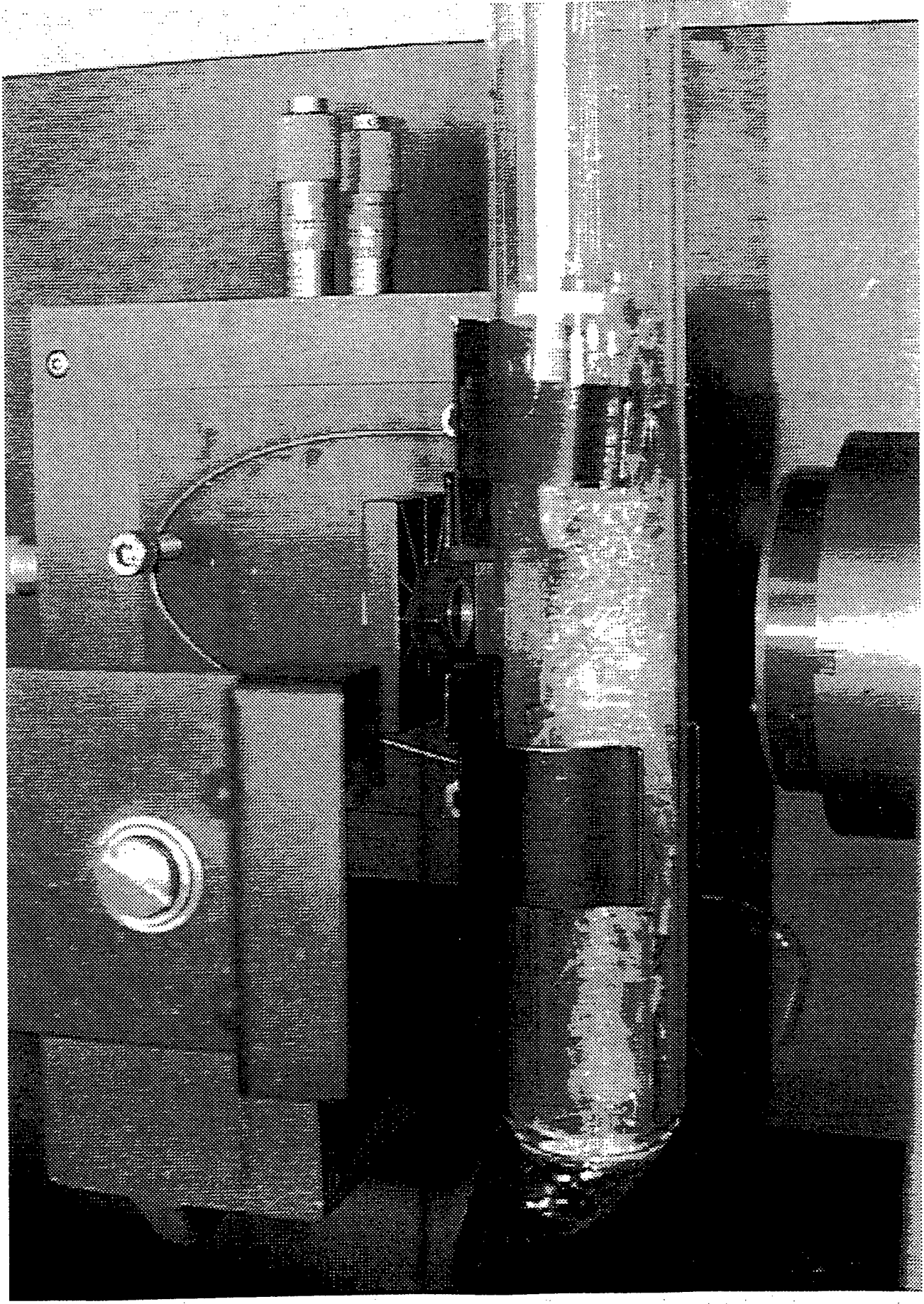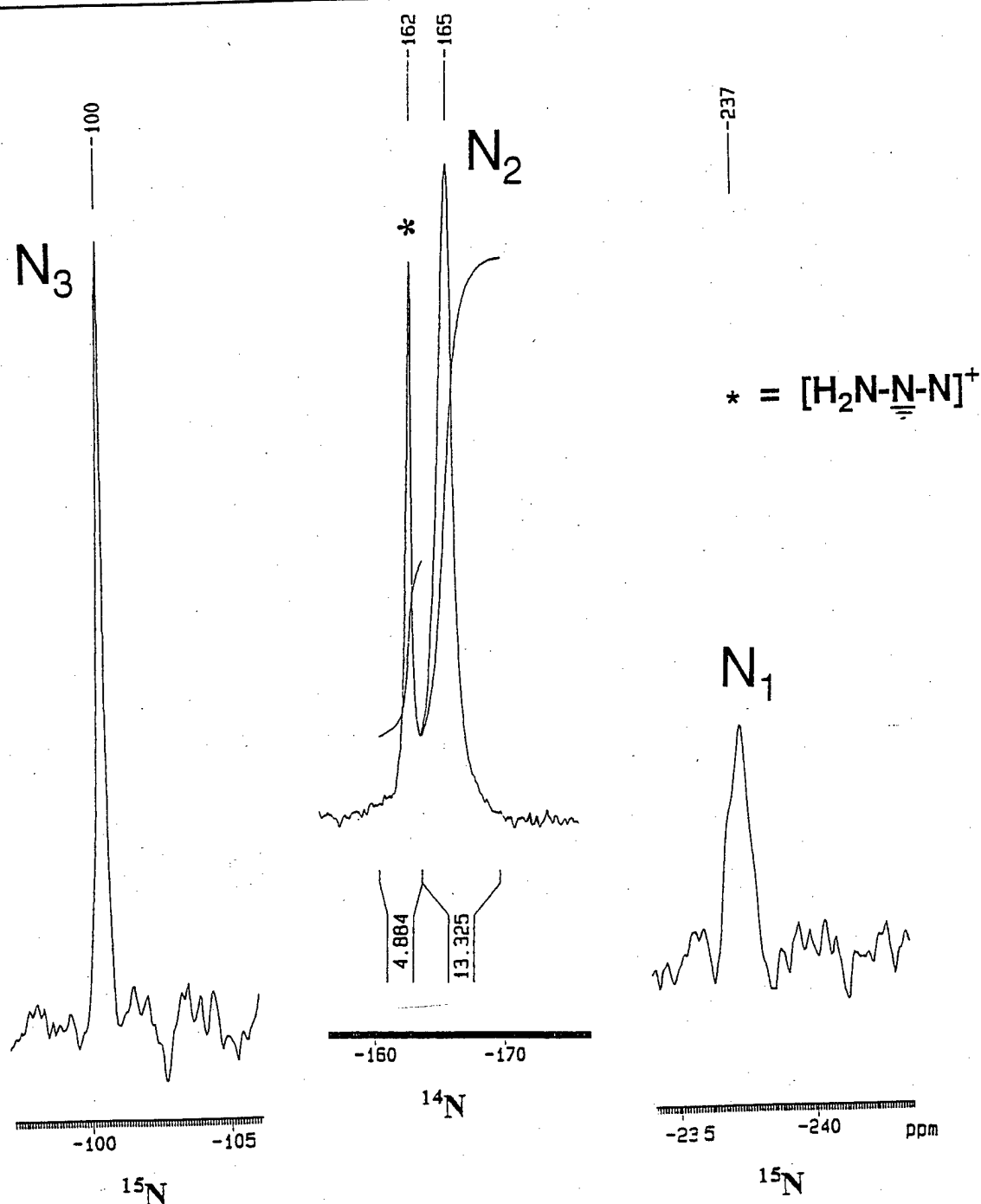
NMR SHIFTS (ppm)	OBSD	CALCD
N_1	-237.3	-235
N_2	-165.3	-166
N_3	-100.4	-95

FORCE FIELD ANALYSIS FOR N_5^+

- TWO MOST IMPORTANT FORCE CONSTANTS
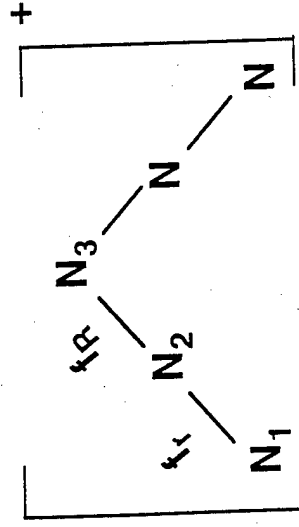
$$f_r = 20.08 \text{ mdyn/Å}$$

$$f_R = 6.59 \text{ mdyn/Å}$$

- TYPICAL FORCE CONSTANT VALUES FOR N-N

  SINGLE BONDS   3.6 mdyn/Å

  DOUBLE BONDS   10.2 mdyn/Å

  TRIPLE BONDS   22.4 mdyn/Å

- THUS N(2)-N(3) HAS BOND ORDER OF ~1.5 AND IS RESONANCE

  STABILIZED AT THE EXPENSE OF N(1)-N(2)

WHAT NEXT?

$$\text{GRAPHITE} \xrightarrow{+ \text{AsF}_5} C_{10}\cdot\text{AsF}_5 \xrightarrow{+ N_2F_4} \text{trans-}N_2F_2 \longrightarrow \text{cis-}N_2F_2 \xrightarrow{+ \text{SbF}_5} N_2F^+SbF_6^-$$

$$N_2F^+SbF_6^- + HN_3 \longrightarrow N_5^+SbF_6^- \xrightarrow[\text{SCALE UP}]{(X10)} N_5^+SbF_6^- \xrightarrow{+ N_3^-} \text{<} \quad \text{METATHESIS} \quad N_5^+N_3^-$$
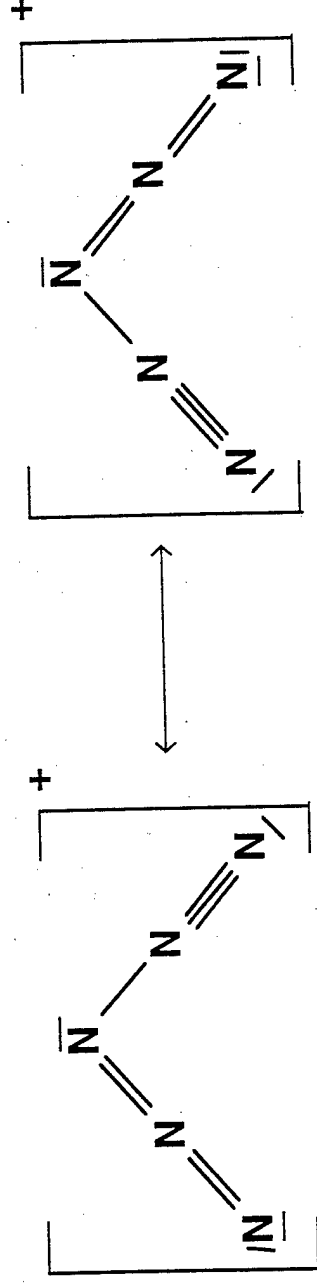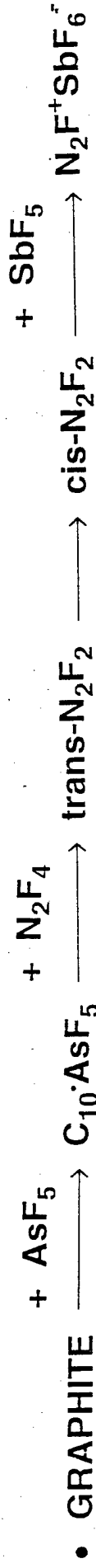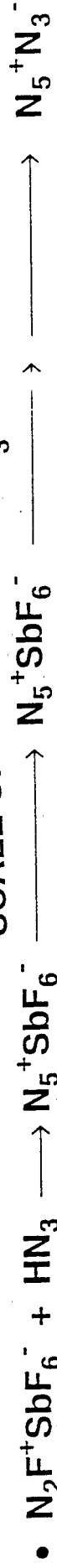
STABILITY TESTS
SAFETY TESTS → MAKE A BETTER POLY-N CATION
$N(N_3)_4^+$, XeN_3^+, etc.

COMPATIBILITY
TEST → MAKE A LARGER POLY-N ANION
$N(N_3)_2^-$, etc.
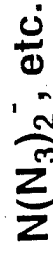
CHARACTERIZATION
SAFETY DATA → SCALE UP → PROCESS IMPROVEMENT → PRODUCTION → TESTING

ESTIMATED ENERGY CONTENT OF $N_5^+N_3^-$

- **HEAT OF FORMATION OF $N_5^+N_3^-$**

  $\Delta H_f^{298} \, N_5^+ \, {}_{(g)} = 351$ kcal/mol   (THIS WORK)

  $\Delta H_f^{298} \, N_3^- \, {}_{(g)} = 43.2$ kcal/mol   (NBS TABLES)

  $U_L \, N_5^+N_3^- \sim 130 \pm 20$ kcal/mol   (ESTIMATE)

  $\Delta H_f^{298} \, N_5^+N_3^- \, {}_{(S)} = 351 + 43 - 130 = 264 \pm 25$ kcal/mol

- **ENERGY DENSITY OF $N_5^+N_3^- \, {}_{(S)} = 2.36$ kcal/g**

- **COMPARISON OF ENERGY DENSITIES (kcal/g)**

O_3	$C(N_3)_3^+N(NO_2)_2^-$	HN_3	$N_5^+N_3^-$	H_2/O_2
0.71	1.42	1.63	2.36	3.21

SUMMARY

- THE FEASIBILITY OF POLYNITROGEN BASED HEDM COMPOUNDS HAS BEEN DEMONSTRATED BY THE SUCCESSFUL BULK SYNTHESIS OF N_5^+

- THE $N_5^+ AsF_6^-$ SALT IS OF SURPRISING STABILITY AND WAS UNAMBIGUOUSLY IDENTIFIED BY VIBRATIONAL AND NMR SPECTROSCOPY OF UNLABELED AND ^{15}N LABELED N_5^+ AND THEORETICAL CALCULATIONS

- THE N_5^+ CATION IS THE FIRST NEW CATENATED HOMOLEPTIC POLYNITROGEN COMPOUND PREPARED IN BULK IN OVER 100 YEARS AND ONLY THE THIRD KNOWN COMPOUND OF THIS TYPE BESIDES ELEMENTAL NITROGEN AND AZIDE

- THEORETICAL CALCULATIONS PLAYED A CRUCIAL ROLE IN THE SUCCESSFUL IDENTIFICATION OF N_5^+ AND DEMONSTRATE THE POWERFUL SYNERGISM OF THEORY AND SYNTHESIS

ACKNOWLEDGEMENT

- DR. MARIO FAJARDO (MASS SPECTRA)

- DR. JOHN STANTON (NMR SHIFT CALCULATIONS)

- MR. ALAN KERSHAW (NITROGEN NMR SPECTRA)

Table 1. Observed and Calculated Nitrogen NMR Data for N_5^+

	chemical shifts,[a] ppm				
	observed[b]		calculated,[c] CCSD(T)/QZP		
	^{15}N	^{14}N	N_1	N_2	N_3
$[^{15}N_1 - {}^{14}N_2 - {}^{14}N_3 - {}^{14}N_{2'} - {}^{14}N_{1'}]^+$	-237.3				
		-165.3[d]	-235	-166	-95
$[^{14}N_1 - {}^{14}N_2 - {}^{15}N_3 - {}^{14}N_{2'} - {}^{14}N_{1'}]^+$	-100.4				

alignment

(a) Chemical shifts are given relative to neat CH_3NO_2 as external standard. (b) The spectra were recorded hydrogen-coupled at -63 °C in anhydrous HF solution which was acidified with AsF_5. (c) An empirical correction of -20 ppm was applied to all calculated values, based on a comparison between the calculated and observed shifts of a number of closely related molecules and ions. (d) The other two resonances are badly exchange broadened and were not detected in the ^{14}N spectrum.

Table 2. Low-temperature Raman and Infrared Spectra of Solid $^{14}N_5^+ AsF_6^-$ and Their Assignments Compared to the Calculated Harmonic Frequencies of Free Gaseous N_5^+

observed freq, cm^{-1} (rel intens)		assignt (point group)		calcd freq^d, (intens)^b	
Raman	IR	$^{14}N_5^+(C_{2v})$	$AsF_6^-(O_h)$	B3LYP	CCSD(T)
-130°C	-196°C				
2271 [44]	2270 m	$v_1(A_1)$		2336 (22)	2229 (13) [215]^c
2211 [8]	2210 s	$v_7(B_2)$		2282 (147)	2175 (105) [42]
	1088 s	$v_8(B_2)$		1167 (141)	1032 (138) [2]
871 [7]	872 w	$v_2(A_1)$		850 (4)	818 (0.5) [5]
	704 vs		$v_3(F_{1u})$		
686 [100]	680 sh		$v_1(A_{1g})$		
672 [17]		$v_3(A_1)$	or part of v	678 (1)	644 (2) [1]
669 [18]			$_1(A_{1g})$ or $v_3(F_{1u})$		
579 [16]	575 w		$v_2(E_g)$		
		$v_5(A_2)$		502 (0)	475 (0) [1]
	420 sh	$v_6(B_1)$		424 (7)	405 (6) [0]
		$v_9(B_2)$		436 (0.6)	399 (1) [0.5]
	394 vs		$v_4(F_{1u})$		
372 [32]	380 sh		$v_5(F_{2g})$		
	360 sh				
209 [44]		$v_4(A_1)$		193 (0.5)	181 (0.3) [6]
127 [55]		lattice vibration			

(a) Using a 6-311 + G(2d) basis set. (b) IR intensities in km/mol; Ra intensities in Å^4/amu. (c) The Ra intensities were calculated at the RHF level.

Table 3. Comparison of the Calculated (B3LYP) and Observed [15]N Isotopic Shifts for N_5^+

N(1)	N(2)	N(3)	N(2)	N(1)	calculated frequencies (shifts), cm^{-1}									observed frequencies (shifts), cm^{-1}					
					$v_4(A_1)$	$v_9(B_2)$	$v_6(B_1)$	$v_5(A_2)$	$v_3(A_1)$	$v_2(A_1)$	$v_8(B_2)$	$v_7(B_2)$	$v_1(A_1)$	$v_2(A_1)$ IR	$v_2(A_1)$ RA	$v_7(B_2)$ IR	$v_7(B_2)$ RA	$v_1(A_1)$ IR	$v_1(A_1)$ RA
14	14	14	14	14	193.1(0)	424.1(0)	436.3(0)	502.4(0)	678.1(0)	850.0(0)	1116.9(0)	2281.7(0)	2336.3(0)	872(0)	871(0)	2210(0)	2211(0)	2271(0)	2271(0)
14	14	15	14	14	191.8(1.3)	422.0(2.1)	436.0(.2)	502.4(0)	677.5(.7)	833.3(16.7)	1138.0(28.9)	2281.2(.5)	2336.3(.1)	858(14)	855(16)	2209.8	2211(1)	2270.8	2271(0)
15	14	14	14	14	190.8(2.2)	422.3 (1.8)	434.7(1.5)	500.7(1.7)	674.4(3.7)	847.4(2.6)	1163.4(3.5)	2259.8(21.9)	2324.5(11.9)	870(2)	869(2)	2189.0(21)	2190(21)	2259.0(12)	2259(12)
14	15	14	14	14	192.6(.4)	419.4(4.7)	430.4(5.8)	496.1(6.3)	670.6(7.5)	846.6(3.4)	1165.0(1.8)	2253.3(28.4)	2331.6(14.8)						
14	14	15	15	14	191.4(1.7)	417.4(6.8)	430.2(6.0)	496.1(6.3)	669.9(8.2)	829.9(20.1)	1136.0(30.8)	2252.9(28.8)	2321.5(14.9)						
15	14	15	14	14	189.6(3.5)	420.2(3.9)	414.5(1.8)	500.7(1.7)	673.8(4.3)	830.6(19.4)	1134.5(32.4)	2259.3(22.4)	2324.4(12.0)						
15	14	14	14	15	192.2(.9)	415.6(8.5)	424.9(11.4)	489.0(13.4)	662.9(15.3)	843.3(6.8)	1163.2(3.7)	2240.1(41.5)	2291.5(44.8)						
15	15	14	14	14	190.4(2.7)	417.3(6.8)	428.8(7.4)	494.6(7.8)	667.1(11.0)	844.1(5.9)	1161.8(5.1)	2222.9(58.7)	2317.3(19.0)						
14	15	14	14	15	190.4(2.7)	417.9(6.2)	428.9(7.4)	494.1(8.3)	666.9(11.2)	844.1(6.0)	1161.5(5.3)	2243.4(38.3)	2297.7(38.6)						
15	14	14	15	14	188.6(4.5)	420.5(3.6)	433.1(3.1)	498.9(3.5)	670.6(7.5)	845.0(5.0)	1159.8(7.0)	2247.4(34.2)	2303.1 (33.2)						
14	15	15	15	14	191.0(2.1)	413.4(10.7)	424.7(11.6)	489.0(13.4)	662.1(16.0)	826.4(23.6)	1134.1(32.8)	2239.7(41.9)	2291.5(44.8)						
15	15	15	14	14	189.2(3.9)	415.2(8.9)	428.6(7.6)	494.6(7.8)	666.5(11.6)	827.2(22.8)	1132.8(34.1)	2222.5(59.1)	2317.1(19.2)						
14	15	15	14	14	189.2(3.9)	415.8(8.3)	428.7(7.6)	494.1(8.3)	666.3(11.8)	827.2(22.9)	1132.5(34.4)	2242.9(38.8)	2297.6(38.7)						
15	14	15	15	14	187.4(5.7)	418.4(5.7)	432.9(3.3)	498.9(3.5)	670.2(8.0)	828.0(22.0)	1130.9(36.0)	2246.9(34.8)	2303.0(33.3)						
15	15	14	14	15	189.9(3.1)	413.7(10.4)	423.3(13.0)	487.2(15.2)	659.3(18.8)	840.7(9.3)	1159.9(7.0)	2217.3(64.3)	2279.7(56.6)						
15	14	14	15	15	188.2(4.9)	415.8(8.3)	427.3(9.0)	492.6(9.8)	663.3(14.8)	841.7(8.4)	1158.2(8.7)	2218.4(63.2)	2288.1(48.3)						
15	15	14	15	14	188.8(4.3)	411.6(12.5)	423.1(13.1)	487.2(15.2)	658.7(19.5)	823.8(26.2)	1130.8(36.1)	2216.9(64.8)	2279.6(56.7)						
15	15	15	14	15	187.0(6.1)	413.7(10.4)	427.1(9.2)	492.6(9.8)	662.8(15.3)	824.7(25.4)	1129.2(37.7)	2218.0(63.7)	2287.9(48.4)						
15	15	14	15	15	187.7(5.4)	411.9(12.2)	421.7(14.6)	485.4(17.0)	655.8(22.4)	838.4(11.7)	1156.6(10.3)	2205.0(76.6)	2257.4 (78.9)						
15	15	15	15	15	186.5(6.5)	409.8(14.3)	421.5(14.7)	485.4(17.0)	655.2(22.9)	821.3(28.7)	1127.4(39.4)	2204.5(77.1)	2257.4(79.0)						

Table 4. Results from the Normal Coordinate Analysis[a] of N_5^+

approx mode description in point group C_{2v}		frequency, cm^{-1} obsd	calcd CCSD(T)(B3LYP)	symmetry force constants[b], CC SDT (B3LYP)				potential energy distribution[a], % (CCSDT)
				F_{11}	F_{22}	F_{33}	F_{44}	
A_1 ν_1	in phase terminal stretches	2270	2229 (2336)	F_{11} 19.573(21.314)				93(1) + 6(2)
ν_2	sym central stretch	872	818 (850)	F_{22} 0.702(.843)	5.546(6.952)			62(2) + 23(3) + 13(4) + 2(1)
ν_3	central bending		644 (678)	F_{33} 0.085(.4137)	1.377(1.535)	1.540(1.427)		39(3) + 33(2) + 23(4) + 5(1)
ν_4	in phase terminal bends	209	181 (193)	F_{44} 0.167(.171)	0.204(.312)	0.120(0.108)	.373(.425)	64(4) + 37(3) - 1(2)
A_2 ν_5	torsion		475 (502)	F_{55} 0.0266(.0281)				100(5)
B_1 ν_6	torsion		405 (424)	F_{66} 0.0236(.0246)				100(6)
B_2 ν_7	out of phase term stretch	2210	2175 (2282)	F_{77} 19.491(21.272)	F_{88}	F_{99}		96(7) + 4(8)
ν_8	asym central stretch	1088	1032 (1167)	F_{88} 1.197(1.359)	4.780(5.927)			95(8) + 4(7)
ν_9	out of phase terminal bends		399 (436)	F_{99} 0.200(.195)	0.085(.159)	.358(.423)		99(9) + 1(8)

(a) The following symmetry coordinates were used for [N_1-N_2-N_3-N_2'-N_1']$^+$: S_1=ν(1-2)+ν(1'-2'); S_2=ν(2-3)+ν(2'-3); S_3=δ(2-3-2'); S_4=δ(1-2-3)+δ(1'-2'-3); S_5=τ(1-2-3-2')+τ(2-3-2'-1'); S_6=τ(1-2-3-2')-τ(2-3-2'-1'); S_7=ν(1-2)-ν(1'-2'); S_8=ν(2-3)-ν(2'-3); S_9=δ(1-2-3)-δ(1'-2'-3). (b) The two most important internal force constants, estimated from the calculated symmetry force constants and the observed frequencies are $f_{(1-2)}$=20.08 mdyn/Å and $f_{(2-3)}$=6.59 mdyn/Å. Streching constants in mdyn/Å, deformation constants in mdyn/Å/rad², and stretch-bend interaction constants in mdyn/rad.